FORWARD OSMOSIS FOR WASTEWATER RECLAMATION: TRACE ORGANIC CONTAMINANTS REMOVAL AND COOLING FOR POST-COMBUSTION CO_2 CAPTURE

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the degree of

Doctor of Philosophy

under the supervision of Long D. Nghiem, Qilin Wang and William E. Price

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This thesis is dedicated to my parents

Liying Liu *and* ***Xiaohong Zheng***

For their endless love, support and encouragement

Certificate of Original Authorship

I, **Lei Zheng** declare that this thesis, is submitted in fulfilment of the requirements of the award of **Doctor of Philosophy**, in the School of Civil and Environmental Engineering at the University of Technology Sydney.

I also certify that the work in this thesis has not previously been submitted for a degree nor it has been submitted as part of requirements for a degree except as fully acknowledged within the text.

This thesis is wholly my own work unless otherwise reference or acknowledged. Any help that I have received in my research and preparation of the thesis has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This research is supported by the Australian Government Research Training Program.

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Research Outcome Summary

Refereed Journal Papers

1) **L. Zheng**, W.E. Price, T. He, and L.D. Nghiem, Simultaneous cooling and provision of make-up water by forward osmosis for post-combustion CO_2 capture. Desalination, 476 (2020), 1-7.
2) **L. Zheng**, W.E. Price, J. McDonald, S.J. Khan, T. Fujioka, and L.D. Nghiem, New insights into the relationship between draw solution chemistry and trace organic rejection by forward osmosis. Journal of Membrane Science, 587 (2019), 1-10.
3) **L. Zheng**, W.E. Price, and L.D. Nghiem, Effects of fouling on separation by forward osmosis: the role of specific organic foulants. Environmental Science and Pollution Research, 26 (2018), 33758-33769.

Submitted and In-preparation Journal Papers

1) **L. Zheng**, K.K. Li, Q.L. Wang, G. Naidu, W.E. Price, X.W. Zhang, and L.D. Nghiem, Low-temperature stripping of CO_2 from aqueous amine-based solvents via integrated direct contact membrane distillation-forward osmosis, Journal of Membrane Science, Submitted.
2) M. Krajewska, **L. Zheng**, M. Szczygielda, L.D. Nghiem, and K. Prochaska, Bio-carboxylic acid recovery from fermentation broth by integrated forward osmosis -reverse osmosis system, Journal of Membrane Science, in preparation.

Conference Presentation

1) **L. Zheng** and L.D. Nghiem, Regeneration of amine-based solvent via integrated direct contact membrane distillation - forward osmosis (DCMD-FO) for post-combustion CO_2 capture. Oral presentation at the *10^th^ International Membrane Science & Technology Conference*, Sydney, 2nd - 6th February 2020.
2) **L. Zheng** and L.D. Nghiem, New insights into the relationship between draw solution chemistry and trace organic rejection by forward osmosis. Oral presentation at the *2nd Green Technologies for Sustainable Water*, Ho Chi Minh City, 1st - 5th December 2019.

3) **L. Zheng** and L.D. Nghiem, Simultaneous cooling and provision of make-up water by forward osmosis for post-combustion CO_2 capture. Oral presentation at the *2nd International Conference on Energy-Efficient Separation*, Melbourne, 27th - 30th December 2019.
4) **L. Zheng** and L.D. Nghiem, Effects of fouling on separation by forward osmosis: the role of specific organic foulants. Oral presentation at the *6th Membrane of Australasia Early Career Researcher Membrane Symposium*, Melbourne, 30th - 1st February 2019.
5) **L. Zheng** and L.D. Nghiem, Effects of fouling and chemical cleaning on the rejection of trace organic contaminants by forward osmosis. Oral presentation at the *9th International Conference in Challenges in Environmental Science & Engineering*, Kaohsiung, 6th - 10th November 2016.

Awards and Prizes

1) First Prize in Three Minutes Short Talk – Best Overall Award at the *2nd International Conference on Energy-Efficient Separation*, 2019, Melbourne.
2) People's Choice Award for Oral Presentation at the *Civil and Environmental Engineering School Research Showcase*, 2019, University of Technology Sydney.
3) People's Choice Award for Oral Presentation at the *Three Minutes Thesis Competition in Faculty of Engineering and Information Technology*, 2019, University of Technology Sydney.
4) Winner of Travel Award, one of 15 student representatives for the research exchange program in Poznan University of Technology, 2019, Poznan.
5) Winner of Travel Award, *6th Membrane Society of Australasia Early Career Researcher Symposium*, 2019, Melbourne.
6) A Prize for Excellence at the *12th Chunhui Chinese Students Innovations and Entrepreneurship Competition*, 2017, Guangzhou.
7) A Prize for Excellence at the *3rd Western China Overseas Hi-tech and High Talents Entrepreneurship Competition (Oceania Division)*, 2017, Sydney.

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List of Abbreviations

Abbreviation	Meaning
AL-DS	Active Layer Facing Draw Solution
AL-FS	Active Layer Facing Feed Solution
BEOP	Biofilm-Enhanced Osmotic Pressure
CA	Cellulose Acetate
CEOP	Cake-Enhanced Osmotic Pressure
COD	Chemical Oxygen Demand
CTA	Cellulose Triacetate
DCMD	Direct Contact Membrane Distillation
DF	Dilution Factor
DI water	Deionized Water
DOC	Dissolved Organic Carbon
DS	Draw Solution
ECP	External Concentration Polarisation
EDX	Energy Dispersive X-ray Spectroscopy
FO	Forward Osmosis
FS	Feed Solution
FTIR	Fourier Transform Infrared Spectroscopy
HA	Humic Acid
HOAc	Acetic acid
ICP	Internal Concentration Polarisation
LC-OCD	Liquid Chromatography with Organic Carbon Detection
LiCl	Lithium Chloride
LMW	Low Molecular Weight
MD	Membrane Distillation
MEA	Monoethanolamine
MPA	Minimum Projection Area
MW	Municipal Wastewater
NaH_2PO_4	Sodium Dihydrogen Phosphate
NaOAc	Sodium Acetate
NF	Nanofiltration
RO	Reverse Osmosis
RSF	Reverse Salt Flux
RSFS	Reverse Salt Flux Selectivity
SA	Sodium Alginate
SG	Sodium Glycinate
SRSF	Specific Reverse Salt Flux
TFC	Thin Film Composite
TOC	Total Organic Carbon
TrOCs	Trace Organic Contaminants
TSS	Total Suspended Solids

Abstract

Water scarcity and global warming are two vexing and intertwined problems with significant impacts on human society and eco-system. Forward osmosis (FO) can potentially be used as an effective tool for wastewater reclamation and alleviating global warming. This study aimed to explore new approaches to deploy FO toward these objectives. This study elucidated the rejection mechanisms of 43 trace organic contaminants (TrOCs) by FO through a systematic investigation of several influencing factors including draw solution chemistry, contaminants species and membrane fouling. This study also demonstrated the viability of FO as an alternative trim cooler in post-combustion CO_2 capture and repetitive CO_2 capture via direct contact membrane distillation - forward osmosis (DCMD-FO) system.

Results from this study revealed that membrane fouling could induce considerable effects on TrOCs rejection via investigations of three specific organic foulants. Municipal wastewater resulted in a more compact fouling cake layer than that caused by humic acid and sodium alginate, which was likely due to large constituents of low molecular weight neutrals and acids. In addition, fouling altered the membrane less negatively charged and less hydrophilic. Steric hindrance caused by the additional filtration cake layer therefore became the dominant rejection mechanism for sulfamethoxazole. However, lower rejection of carbamazepine was likely due to the cake-enhanced concentration polarization.

Through a systemic investigation, results from this study heightened the inherent complexity in TrOCs rejection by FO. Due to the intrinsic bidirectional transport phenomenon, the reverse flux of proton (or hydroxyl radical) could alter the feed solution pH, which governed the separation of ionizable TrOCs. In addition, variation in hydrated radius of draw solution resulted in the sharp contrast in terms of reverse salt flux (NaCl: 33 g/m^2h; LiCl: 2 g/m^2h) and therefore different ionic strength of feed, thus the corresponding electrostatic interaction. Charged compounds generally exhibited higher rejections than neutral ones by the clean membrane, which indicated that electrostatic interaction rather than steric hindrance was the dominant rejection mechanism.

Intrinsic osmotic driving force also enlightened this study to apply FO as an alternative to a trim cooler in post-combustion CO_2 capture. Regenerated amine-based solvents, such as glycine, sodium glycinate, and monoethanolamine (MEA) were successfully used as the draw solution to extract water from treated effluent or seawater, which could provide the make-up water for CO_2 capture. Glycine showed a higher water flux, a lower reverse salt flux and specific reverse salt flux than sodium glycinate and MEA in both membrane orientations, thus was selected for further investigations.

A higher water flux but with considerable flux decline were observed when active layer faced draw solution. Temperature increase in draw solution could alter thermodynamics properties of glycine, thus, resulting in an increase of reverse salt flux. It enhanced water flux due to the diminishing concentrative internal concentration polarisation. On the other hand, changes in water flux were insignificant when active layer faced feed solution even as temperature increased. It appears that temperature increase was likely to aggravate the severity of dilutive internal concentration polarisation and offset the growth of osmotic pressure. Despite of the lower water transportation from seawater than treated effluent due to the less osmotic gradient, seawater could also be as an alternative cooling source and desalinated simultaneously.

This study also demonstrated 85 and 89% of re-absorption capacities for MEA and sodium glycinate in a hybrid DCMD-FO system respectively via the low regeneration temperature. The DCMD achieved respective 33.6 and 33.2% of desorption efficiency for MEA and sodium glycinate at 80 °C. Unlike negligible change caused by sodium glycinate, MEA resulted in either increase or decrease of hydrophobicity for each MD membrane, thus a partial wetting as well. Water production declines were observed for both solvents due to the membrane wetting. However, the high solvent rejection indicated that DCMD resulted in the negligible amine loss.

Regenerated MEA and sodium glycinate resulted in the contrast water flux when deionised water was used as the feed (MEA: 27 L/m^2h, Sodium glycinate: 14 L/m^2h). They both whereas showed a similar water flux (15 L/m^2h) when treated effluent was used as the feed. In addition, sodium glycinate presented a smaller reverse salt flux than that of MEA for both deionised water and treated effluent. A particular membrane structure may lead to the disparity in water flux. More research work is required for the cost-effective CO_2 capture based on membrane system.